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(54) ACYLATED DERIVATIVES OF UREA AND THEIR USE AS HARDENERS FOR POLYMERIC MATERIALS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hardeners for polymeric materials.

According to the present invention there is provided a compound of the general formula:

$$R^3HC{=}CR{-}CO{-}NR^2{-}CO{-}NH{-}CO{-}CR{=}CHR^3$$

wherein each R is a hydrogen atom or an aliphatic or aromatic radical, and R^2 and each R^3 is a hydrogen atom or an alkyl radical having up to 8 carbon atoms.

Hardenable natural and synthetic materials can be hardened and so rendered more resistant to the swelling effects of aqueous solutions, even at elevated temperatures, by the new class of compounds. The new hardening compounds harden polymers such as gelatin or primary amine-containing synthetic compounds in various forms such as solutions, emulsions, or layers in a rapid, well-controlled manner without undesirable after-hardening. The new hardeners are non-wandering.

Although preferably mixed with or added to said polymers in emulsions, they can be added in any other suitable manner with similarly good results.

The compounds of this invention are of a low molecular weight, this generally being in the range of from 168 to approximately 400, and preferably being less than 320. They are comprised of two aliphatic, ethylenically-unsaturated acyl radicals, for example, acryloyl or crotonyl, linked together through an intervening carbonyl and nitrogen-containing bivalent moiety such as urea. The acyl radicals can be further substituted as shown in the foregoing formula by lower alkyl groups, e.g., methyl, ethyl, propyl, butyl. The bivalent moiety can contain a substituent on one nitrogen atom. Suitable substituents include lower alkyl radicals, such as, methyl, ethyl, propyl, isopropyl and butyl. The ethylenically unsaturated acyl radicals can be unsubstituted in the alpha position to the carbonyl group or can contain substituents such as lower alkyl (e.g., alkyl of from 1 to 8 carbon atoms and preferably those of 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl and butyl) groups or aromatic groups such as aryl (e.g. phenyl) groups.

The compounds of this invention, which have been found to be especially useful in the hardening of compositions of matter comprising gelatin, can be used in any suitable hardening concentration, concentrations of from 0.5 to 10 per cent based upon the weight of the hardenable material being satisfactory in many instances. The preferred range for hardening gelatin is from 0.67 to 3 per cent. These compounds are particularly useful for hardening photographic gelatino silver halide emulsions. The compound may be incorporated directly in the emulsion during its preparation or it may be introduced into a coated layer of the emulsion by treating the layer during processing with a bath, such as an acid-fixing bath, containing the compound. Although not

readily soluble in water, the compounds are useful in aqueous acid solutions in a wide range of concentrations.

The new compounds of this invention can be prepared by the reaction of an unsaturated acyl isocyanate, of the general formula $R^3CH{=}CR{-}CO{-}NCO$ for example, acryloyl isocyanate, with an acrylamide of the general formula $R^3CH{=}CR{-}CO{-}NHR^2$, R, R^2 and R^3 being as already defined. The presence of a free-radical polymerization inhibitor is desirable and useful examples of such compounds are *m*-dinitrobenzene and *p*-dimethylaminoanisole. These inhibitors will not react with the isocyanate since they do not contain active hydrogen atoms and they may be used in any concentration sufficient to prevent unwanted polymerization. The compounds of this invention can be prepared in other ways, for example, by the reaction between a haloacylisocyanate with an amide and the subsequent dehydrohalogenation of the reaction product. Further, as shown by Examples 2 and 3 it is also possible to prepare these new compounds according to known methods by foregoing the step of isolating the intermediate acryloyl isocyanate, which can be formed by reaction between silver cyanate and a compound of the general formula

$$R^3CH{=}CR{-}COCl,$$

prior to reaction with the acrylamide.

Suitable solvents which can be used in the aforementioned reactions include 1,2-dichloroethane, chloroform and trichloroethane, but any such inert organic solvent can be satisfactorily used, provided it has a low boiling range (60—100°C) in order to prevent polymerization of the acrylic moieties. The use of catalysts is optional.

All such reactions can be conducted in the chosen organic solvents at moderate temperatures and since the reactions are not pressure dependent, can be conducted at superatmospheric or subatmospheric pressures. As is obvious to one skilled in the art, the specific reaction conditions depend upon the particular reactants used.

The compounds of this invention can be used effectively with hardenable materials in general but are most advantageously used with natural or synthetic polymers used as vehicles or binders in preparing photographic materials. Materials which can be hardened according to the practice of this invention include gelatin, colloidal albumin, proteins, dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials as exemplified by amine-containing polymers of alkyl acrylates, methacrylates, acrylic acid, sulphoalkyl acrylates or methacrylates and maleic acid.

The hardening agents described herein can be used in various kinds of photographic emulsions, including orthochromatic, panchromatic, and infrared emulsions, and X-ray and other non-spectrally sensitized emulsions. They can be added to the emulsions before or after the addition of any spectral sensitizing dyes which may be used and are effective in sulphur and gold sensitized silver halide emulsions.

The materials hardened with the hardeners of this invention can be coated on a wide variety of supports, including those generally employed for photographic materials, as exemplified by cellulose nitrate, cellulose acetate, polyvinyl acetal, polystyrene and polyethylene terephthalate films, glass, metal, wood and paper. The latter can be coated with α-olefin polymers, particularly polymers of α-olefins containing 2—10 carbon atoms, such as polyethylene, polypropylene and ethylene butene copolymers.

In addition to the hardening agents of the invention photographic emulsions and materials can also contain the usual photographic addenda such as spectral sensitizers, speed increasing materials, other hardeners and plasticizers.

Emulsions hardened by the compounds of the invention can be used in photographic materials intended for colour photography including those containing colour-forming couplers, those to be developed by solutions containing couplers or other colour-generating materials, and those of the mixed-packet type.

The silver halides in the photographic emulsions can be any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide and silver chloroiodide. The emulsions can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images predominantly inside the silver halide grains.

Hardened emulsions obtained in accordance with this invention can be used in materials for diffusion transfer processes. In some of these processes undeveloped silver halide in non-image areas of an exposed and developed emulsion layer is complexed to form a water-soluble compound which diffuses to a receiving layer in which it decomposes to form a positive metallic silver image. In other of these diffusion transfer processes, the final image is produced by diffusion of a developer, oxidized developer, coupler or dye, from an exposed and developed light-sensitive layer to a second layer in close proximity thereto. It is particularly advantageous to employ the hardeners of this invention in applications where the absence of wandering and/or after-hardening is advantageous.

The invention is illustrated by the following Examples. "Parts" referred to therein are by weight.

EXAMPLE 1

Preparation of N,N'-Diacryloylurea (Compound 1)

9.7 Parts of acryloyl isocyanate is added to 10 parts of acrylamide and 0.5 parts of m-dinitrobenzene in 100 parts of 1,2-dichloroethane. This mixture is refluxed under nitrogen for longer than 15 hours. The acryloyl isocyanates are well known and previously described by Lieser and Kemner in Ber. 84, 1 (1951). A small amount of solid precipitate is filtered from the hot resulting solution. The filtrate is cooled to about −20°C. The resulting precipitated product is collected on a filter and dried under vacuum. The resulting crude, dry solid [(11 parts) having an m.p. of 111—130°C.] is tumbled with 200 parts of water for about an hour, collected on a filter and vacuum dried. The dry solid is then dissolved in 125 parts of boiling 1,2-dichloroethane with rapid stirring. After filtration and cooling, the solid product is collected on a filter and dried to yield 7 parts of final product having an m.p. of 142—144°C.

EXAMPLE 2

Preparation of N - acryloyl - N' - methacryloylurea (Compound 2)

4.5 Parts of acrylyl chloride is added dropwise, under nitrogen over a period of about 1 hour, to a stirred, ice cooled suspension of 15 parts of silver cyanate and 0.2 parts of m-dinitrobenzene in 50 parts of 1,2-dichloroethane. The mixture is allowed to reach ambient temperature and stirred 15 hours. The mixture is then centrifuged to remove suspended matter and to the supernatant liquid is added 4 parts of recrystallized methacrylamide and 0.2 parts of m-dinitrobenzene. This mixture is heated to boiling on a steam pot with stirring under nitrogen. Heating is continued for 4 hours. This mixture is filtered hot and cooled in a freezer for about 15 hours. The resulting solid is filtered, washed, and vacuum dried. The dry solid is tumbled with 20 parts of water, filtered, and vacuum dried. The white dry solid is recrystallized from 3 parts 1,2-dichloroethane containing 0.02 parts dinitrobenzene in a yield of 0.4 parts and has a melting point of 130—133°C.

EXAMPLE 3

Preparation of N-Methyl-N,N'-Diacryloylurea (Compound 3)

A mixture of 50 parts of 1,2-dichloroethane, 15 parts of silver cyanate and 0.1 parts of *m*-dinitrobenzene is stirred in an ice-bath under nitrogen while 4.5 parts of acrylyl chloride is added dropwise over a period of one hour. This mixture is stirred for 15 hours at ambient temperature and is then filtered.

The filtrate is treated with 4.2 parts of N-methyl acrylamide and 0.2 parts of m-dinitrobenzene and then heated for 6 hours on a stream bath under nitrogen before being filtered hot. Cooling for 15 hours in a freezing compartment gave no precipitation. The solution is evaporated to dryness on a Rinco apparatus and the resulting viscous cooled in a freezing unit where it partially solidifies. The precipitate is filtered and tumbeld with 2.5 parts of water. The insoluble material is filtered off and vacuum dried. It is recrystallized from hot hexane yielding 0.2 parts of a light yellow solid with a melting point of 175—177°C.

EXAMPLE 4

Compound 1 (see Example 1) was added to bone gelatin at a concentration of 1 per cent based on the weight of gelatin and the resulting solution coated on a poly(ethylene terephthalate) film support. A control sample containing no hardener was also prepared.

A sample of each film coating was tested for hardness both fresh and after 3 days' incubation at 120°F., 50 per cent relative humidity, by immersing in "Kodak" DK—50 developer at 25°C. for 3 minutes ("Kodak" is a registered trade mark) and measuring the increase in thickness. The percentage swell of the gelatin layer was calculated therefrom, and the results were as follows:

Film Coating	Concentration Based on Weight of Gelatin	% Swell Fresh	3 Days Upon Incubation
Control	0	1300	1210
Compound 1 (N,N'-diacryloylurea)	1%	530	535

EXAMPLE 5

Compound 1 was added to a high speed photographic silver bromoiodide emulsion panchromatically sensitized with a cyanine dye. The emulsion and a control sample containing no hardener were coated on poly(ethylene terephthalate) film support at a coverage of 340 mg. of silver and 772 mg. of gelatin per square foot. Each sample was tested for hardness as outlined in Example 4 with the following results:

Film Coating	Concentration Based on Weight of Gelatin	% Swell Fresh	After 3 day's Incubation at 120°F., 50% Relative Humidity
Control	0	965	870
Compound 1	1%	490	470

EXAMPLE 6

N-Acryloyl-N'-methacryloylurea (Compound 2) and N-methyl-N,N'-diacryloylurea (Compound 3) were tested as hardeners by the procedure described in Example 5 except that the samples were immersed in water, rather than developer. The results are as follows:

Film Coating	Concentration in % by weight Based on weight of Gelatin	Percent Swell in Water After 3 Days' Incubation at 120°F. and 50% Relative Humidity
Control	—	720
Compound 2	1%	550
"	3%	470
"	6%	360
Control	—	590
Compound 3	1%	290
"	3%	210
"	5%	190

EXAMPLE 7

Compound 1 was added to separate portions of a photographic emulsion as described in Example 4. For comparison purposes similar samples were coated using the following hardeners: formaldehyde, N,N'-bis(chloroacetyl) urea, (see British Patent Specification 990,275); N-acryloyl-N'-chloroacetyl urea, and methylenebisacrylamide, (see British Patent Specification 994,869).

Each of these hardening compounds was added in optimally effective hardening concentrations, to separate portions of a photographic emulsion of the type described in Example 4, samples of coatings of these were tested for hardness as described in that Example.

In addition, a sample of each coating was exposed on an "Eastman" IB Sensitometer, processed for five minutes in "Kodak" DK—50 developer, fixed, washed and dried ("Eastman" and "Kodak" are registered trade marks). The results obtained were as follows:

Hardener	% Concentration based on Weight of Hardenable Material	% Swell: Fresh	% Swell: After 2 Weeks Incubation at 120°F., 50% Relative Humidity	Sensitometric Results: Relative Speed	Sensitometric Results: γ	Sensitometric Results: Fog	After 2 Weeks Incubation: Relative Speed	After 2 Weeks Incubation: γ	After 2 Weeks Incubation: Fog
Control (None)	—	965	870	100	1.30	0.07	107	1.09	0.06
N,N′-diacryloylurea	1	490	470	102	0.92	0.10	118	0.97	0.12
Formaldehyde	0.5	380	430	80	0.89	0.05	85	0.80	0.06
N-acryloyl-N′-chloroacetylurea	3	650	520	112	1.12	0.09	112	0.97	0.12
N,N′-bis(chloroacetyl)-urea	10	390	520	129	1.22	0.08	89	1.35	0.08
Methylenebisacrylamide	1	1000	650	129	1.43	0.08	107	0.88	0.08

Example 8

Compound 1 (N,N′-diacryloylurea) was added to a gelatin solution containing physical development nuclei at a concentration of 6% by weight based on the weight of the gelatin and coated as a layer on a cellulose acetate film support. Over this layer was coated a layer of gelatin, similarly hardened with Compound 1. The material obtained was then incubated for 3 days at about 70°F. and 50% relative humidity. The coatings were next overcoated, first with an unhardened gelatino-silver bromoiodide emulsion and then with an unhardened protective gelatin layer, and the resulting material incubated at 120°F. and 50% relative humidity for weeks. The coatings were exposed and processed by immersion for 20 seconds at 90°F. in a monobath having the formula:

Water	700.0 ml.
Sodium sulphite (anhydrous)	60.0 grams
Sodium carbonate (monohydrate)	21.6 „
4,4-dimethyl-1-phenyl-3-pyrazolidone	2.5 „
Hydroquinone	10.0 „
Sodium thiosulphate (pentahydrate)	65.0 „
pH is adjusted to 11.0 to 11.1 with 45% (by weight) aqueous potassium hydroxide (7.13-diethianonadecane-1,19-bis-pyridinium-p-toluenesulphonate)	0.6 gram
Water to equal	1.0 litre

The unhardened layers were washed off in about 10 to 30 seconds using water at a temperature of about 120°F. (the wash temperature can vary from 70°F. to 140°F.) The water was sprayed over the material and easy removal of the unhardened gelatin layers was accomplished by peeling off the unhardened gelatin layer by moderate pressure along the material. This result demonstrated that the hardener remained in the layers in which it was incorporated and did not migrate into the unhardened core layers.

Similar results are obtained when the hardeners of the invention are employed in photographic emulsions having as a binder a mixture of a synthetic polymer and gelatin. One example of such a binder contains 3 parts of polymer and 1 part of gelatin by weight, the polymer being a copolymer of 80% (by weight) ethylacrylate and 20% acrylic acid. Such a binder can suitably be coated at 500—1000 mg. per square foot. Another example of such a binder contains a copolymer of 90% (by weight) butylacrylate and 10% acrylic acid.

Non-light-sensitive and light-sensitive photographic materials comprising a support bearing a plurality of gelatin-containing layers one of which is substantially unhardened and another of which is hardened with a compound of the present invention, the hardened layer or layers being between the support and the substantially unhardened layer, and processes for their manufacture, are described and claimed in our Application No. 53118/68 (Serial No. 1259608), and we make no claim to such materials or processes for their manufacture herein.

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

1. A compound of the general formula:

$$R^3HC{=}CR{—}CO{—}NR^2{—}CO{—}NH{—}CO{—}CR{=}CHR^3$$

wherein each R is a hydrogen atom or an aliphatic or aromatic radical, and R^2 and and R^3 is a hydrogen atom or an alkyl radical having up to 8 carbon atoms.

2. A compound according to Claim 1 wherein each R is an alkyl radical having up to 8 carbon atoms or an aryl radical.

3. N,N′-Diacryloylurea.

4. N-Acryloyl-N′-methacryloylurea.

5. N-Methyl-N,N′-diacryloylurea.

6. A composition which comprises a hardenable polymeric material and in which has been incorporated a compound according to any of the preceding claims.

7. A composition according to Claim 6 wherein the polymeric material comprises gelatin.

8. A composition according to Claim 6 or 7 wherein the polymeric material is synthetic and contains amino groups.

9. A composition according to any of Claims 6 to 8 which is a photographic silver halide emulsion.

10. A composition according to any of Claims 6 to 9 which contains from 0.5 to 10.0 per cent by weight of the compound based on the weight of the hardenable polymeric material.

11. A composition according to any of Claims 6 to 10 which is an aqueous coating composition.

12. A method of making a non-light-sensitive or light-sensitive photographic material which comprises coating a support with a layer of a composition according to Claim 11.

13. A non-light-sensitive or light-sensitive photographic material which comprises a support bearing a layer of a composition according to any of Claims 6 to 10.

14. A method of hardening a layer of

hardenable polymeric material which comprises treating the layer with an acidic aqueous solution of a compound according to any of Claims 1 to 5.

15. A method of making a compound as claimed in Claim 1 which comprises reacting a compound of the general formula

$$R^3CH=CR—CO—NCO$$

with a compound of the general formula $R^3CH=CR—CO—NHR_2$, wherein the groups R, R^2 and R^3 are as defined in Claim 1, in the presence of a free-radical polymerization inhibitor.

16. A method according to Claim 15 wherein the compound of the formula $R^3CH=CR—CO—NCO$ is formed in the reaction mixture from silver cyanate and a compound of the general formula

$$R^3CH=CR—COCl.$$

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